Contribution of Atmospheric Deposition to Pesticide Loads in Surface Water Runoff

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Abstract

A 3.5-year study was conducted to determine the significance of atmospheric deposition to the pesticide concentrations in runoff. Both wet and dry atmospheric depostion were collected at six sites in the central Sar Joaquin Valley, California. Wet deposition samples were collected during individual rain events and dry deposition samples were collected for periods ranging from three weeks to four months. Each sample was analyzed for 41 currently used pesticides and 23 transformation products, including the oxygen analogs of nine organophosphorus (OP) insecticides. Ten compounds in rainfall and 19 in dry deposition were detected in at least 50% of the samples. The herbicides dacthal, pendimethalin, simazine, and trifluralin, and the insecticides carbaryl, chlorpyrifos, and diazinon, were the most frequently detected pesticides in both rainfall and dry deposition. The oxygen analog concentrations (maximum/median) of chlorpyrifos $(1.83/0.213 \text{ micrograms/Liter } [\mu g/I], n = 70) \text{ and diazinon } (2.74/0.327 \ \mu g/L)$ n = 50) in rainfall were at times equivalent to or greater than the parent concentrations. A comparison of the depositional amounts (micrograms per square meter) showed that the magnitude of dry deposition could be as much as 40% higher than wet deposition for some pesticides and that the predominant depositional phase was related to the physical and chemical properties of the pesticide. In a small urban watershed, however, 68% of the diazinon in the runoff could be attributed to rainfall. The more water soluble pesticide—carbaryl, metolachlor, napropamide, and simazine—also showed this trend. Malathion was detected in the runoff water, but not in any rainfall sample. Chlorpyrifos, dacthal, pendimethalin, and trifluralin, compounds with water solubilities less than 1.25 x 10⁻³ moles/m³ and log soil sorbtion coefficient (K_{OC}) values of greater than 2.2, had higher rainfall concentrations than the runoff water and were presumed to be partitioning

Introduction

The atmosphere is an important component of the hydrologic cycle that is often overlooked in many pesticide environmental fate studies. Pesticides have been recognized as potential air pollutants since the mid-1940s. Numerous studies have documented how pesticides drift off-site during and after the application process. Other studies have documented the processes that govern pesticide movement and distribution in the environment (Majewski and Capel, 1995).

onto the suspended sediments and organic matter on the ground.

During and after their application, many pesticides move off the intended target area and can contaminate local rivers and streams. Atmospheric deposition of pesticides is most likely to affect stream water quality during runoff events when precipitation and direct surface runoff are the major sources of streamflow. Locally high concentrations of pesticides in rain and air are seasonal, are correlated to local use, and usually occur during the spring and summer. However, high concentrations of OP pesticides also can occur in rain, air, and fog during the fall and winter in areas such as the stone-fruit orchards in California's Central Valley. Diazinon and chlorpyrifos are among the OP insecticides that are detected most often in the air, rain, and fog in this region of the Central Valley.

Historically, chemical and bioassay monitoring of surface water have shown that pesticides in the San Joaquin River can occur at concentrations that are toxic to sensitive aquatic organisms. Toxicity appears to be caused by pesticides in storm runoff, irrigation tail water, runoff from orchards, and urban runoff (Kuivila and Foe, 1995).

Section 303(d) of the Clean Water Act requires states to identify waters that do not or are not expected to meet applicable water-quality standards with technology-based control alone. The Act also requires states to establish a priority ranking for waters on the 303(d) list of impaired waters and to establish Total Maximum Daily Loads (TMDLs) for those listed waters. Essentially, a TMDL is a planning and management tool intended to identify, quantify, and control the sources of pollution within a given watershed to the extent that water-quality objectives are achieved, and the beneficial uses of water are fully protected. The lower San Joaquin River is listed in California's Clean Water Act Section 303(d) of impaired waters because of elevated concentrations of chlorpyrifos and diazinon.

The two studies presented here are part of a larger U.S. Geological Survey program designed to identify all sources of pesticides in the San Joaquin River watershed. The results will be used by the California Regional Water Quality Control Board to evaluate the current Best Management Practices (BMPs); and the BMPs will be modified where necessary to reduce OP pesticide loading in surface waters in the San Joaquin River.



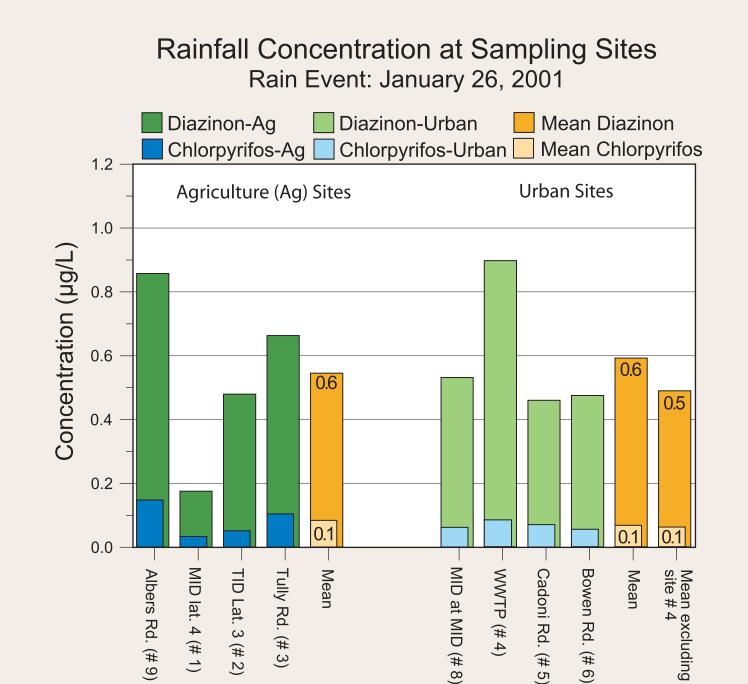
Acknowledgments

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2001 Sampling (Wet Deposition)

Rain Event: January 26, 2001

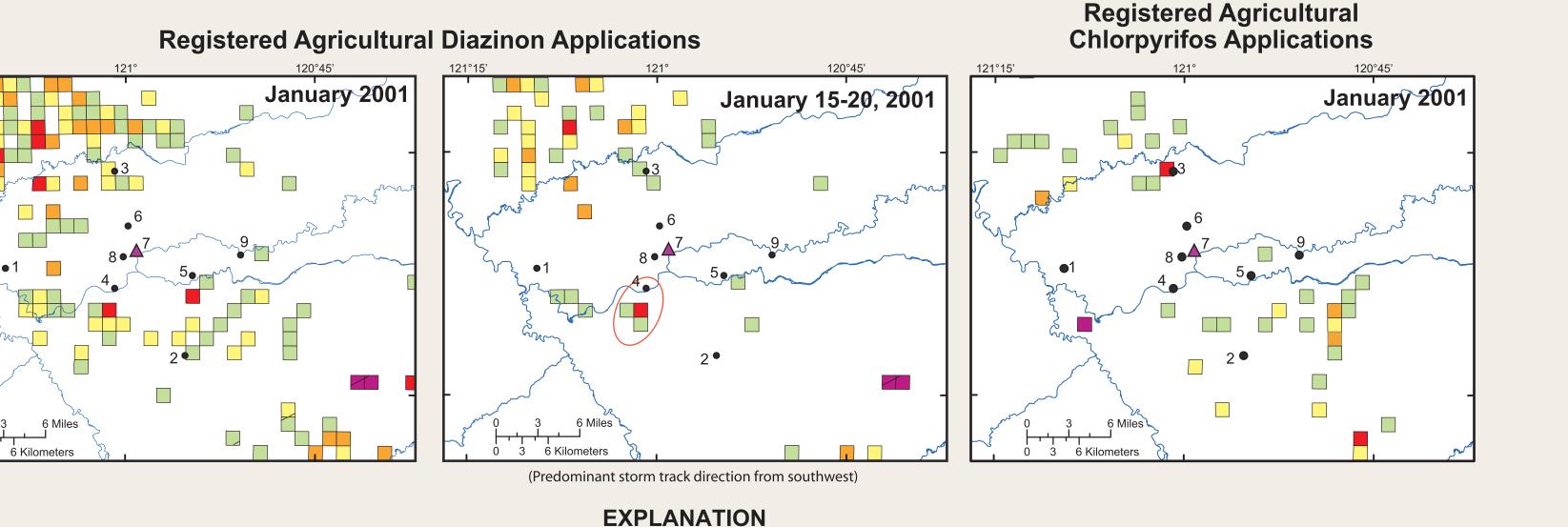
Only one significant rainfall event occurred during the 2001 sampling time frame. The storm event on January 26 was a frontal system that moved into the study area from the southwest. The average event rainfall at all sites was about 1.3 cm.



The concentrations of chlorpyrifos or diazinon at each urban sampling site were similar, with the exception of concentrations at site 4, which were substantially higher. This site, however, was downwind of a major diazinon application the previous week, which probably influenced the results (see encircled area below).

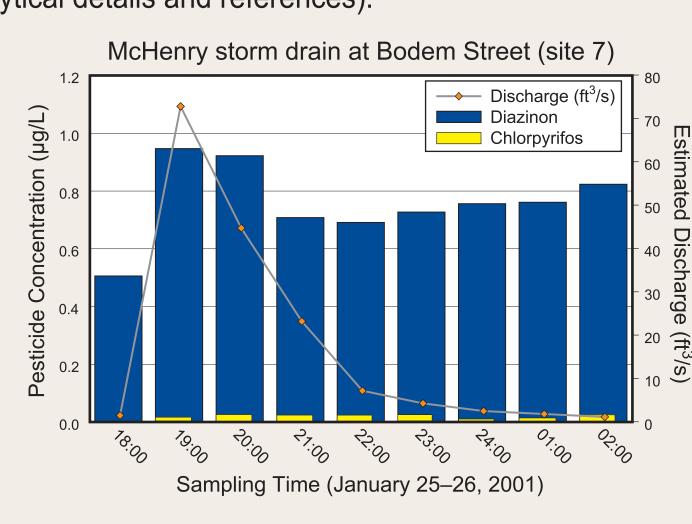
The chlorpyrifos and diazinon results for the agricultural sites were highly variable and reflected their proximity to orchards and local dormant spray operations (See diazinon and chlorpyrifos application area maps below).

The mean chlorpyrifos and diazinon concentrations at the urban and the agricultural sites were nearly equivalent, indicating that the overall atmospheric burden in the region was fairly similar during this event, even though the concentrations at the agricultural sites were variable. It is unknown how much, if any, urban applications occurred in January and if they influenced the results.



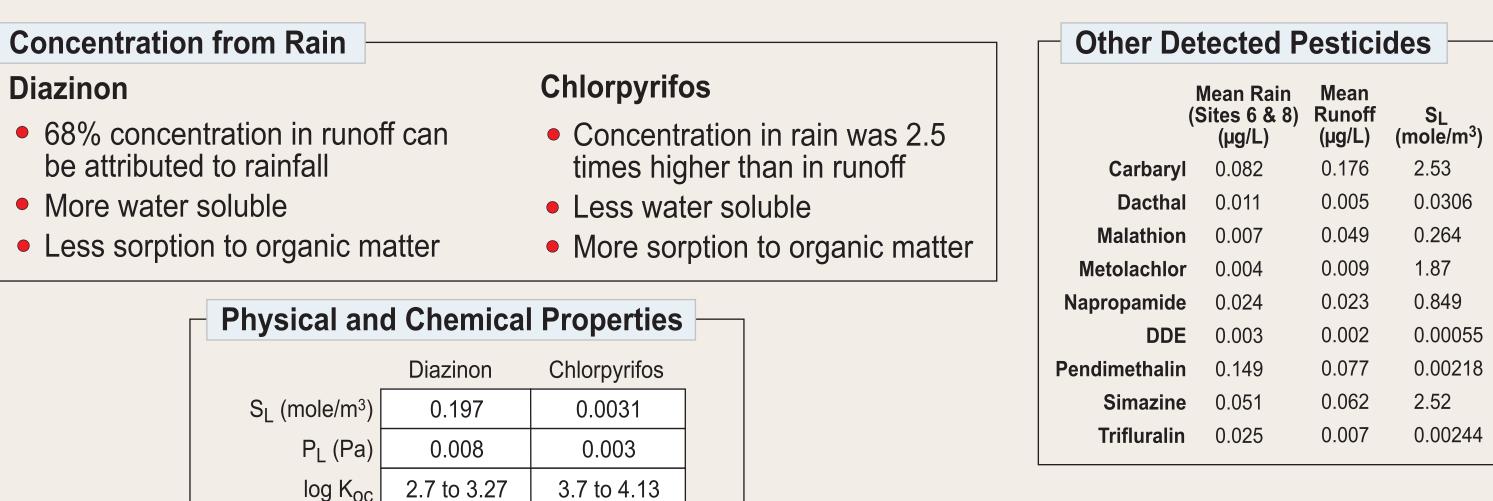
Hourly runoff water samples were collected throughout the event at one storm drain located at the bottom of a small urban watershed (site 7). These samples were filtered and then analyzed for the same constituents as the rainfall samples (see Methods Section for analytical details and references).

0–25 25–50 50–100 100–200 200–450 • Sampling site ▲ Storm drain site



When comparing the mean concentrations in rainfall (sites 6 and 8 were used) to those in the runoff, it was found that the rainfall contributed 68% of the diazinon in the runoff, whereas the chlorpyrifos concentration in the rainfall was 2.5 times higher than in the runoff. These results can be explained using the physical and chemical properties of these insecticides. Since the runoff samples were filtered, and the filters were not analyzed, it can be concluded that most of the chlorpyrifos had been sorbed onto the suspended particulate matter. This behavior was also seen for the several other pesticides detected in both the rain and runoff samples, such as dacthal, pendimethalin, and trifluralin.

P_I, subcooled liquid phase vapor pressure; S_I, water solubility; K_{OC}, soil absorbtion coefficient)



Summary: 2001 Sampling

- Detected pesticide concentrations in rainfall at the urban sites were fairly uniform, with the exception of site 4 that was located immediately downwind of recent orchard pesticide applications.
- Detected pesticide concentrations at the agricultural sites were variable, but were correlated with proximity to orchards and recent pesticide applications.
- Mean concentrations of both chlorpyrifos and diazinon in agricultural and urban rainfall were nearly identical, indicating that the overall atmospheric burden in the region was fairly similar during this event.
- Many of the same pesticides detected in rainfall were also detected in the runoff from a small urban watershed.
- It is likely that pesticides applied in agricultural areas are drifting into the urban environment, but it is unknown how many, if any, urban applications occurred during this study and contributed to the observed urban concentrations.
- Rainfall can contribute significantly to pesticide concentrations in runoff for some compounds, depending on their physical and chemical properties.

Objectives (2001)

Sampler Types

Rain Sampling

Dry Deposition

To collect rainfall samples at urban and agricultural locations in the Modesto area during the orchard dormant spray season (January through February 2001) and to collect runoff samples from an urban storm drain during a rain event.

Four urban and four agricultural sites were located throughout the Modesto study area. The urban sites were located throughout the Modesto metropolitan area—downtown (site 8), an industrial area (site 5), a new residential development (site 4), and an established residential area (site 6). These sites were selected to include a variety of urban land uses and to show the occurrence and distribution of the pesticide content in rainfall.

surrounding the Modesto metropolitan area. Three of the sites were in areas where the predominant land use is orchards—sites 2, 3, and 9. Site 1 was located where the predominant land use is alfalfa. All the agricultural sites, with the exception of site 2, were located away from orchards to minimize any direct influence.

2001 – 2004 Sampling Sites, San Joaquin Valley, California

0 5 10 Kilometers

32-cm diameter Teflon-lined or stainless steel funnels were placed at each

sampling site for no more than 24 hours before a rain event occurred. The

samples were collected within 24 hours of the end of the event. The funnels

funnel-bottle assembly was supported by an appropriate length of plastic

irrigation pipe attached to a small wooden table. The autosamplers used

Chicken wire covered each funnel to intercept large debris, birds, and other

wildlife from entering the collection area. The funnels were exposed to the

screen was removed, and about 50 mL of organic free water from a squeeze

atmosphere from three weeks to several months. At collection, the wire

bottle was used to rinse deposited material off the sides of the funnel.

followed by a rinse using about 50 mL of a 50:50 mixture of hexane:ethyl

Each soil box was about 1-m square and divided in half down the center.

a composite mixture of soil taken from each of the six sampling locations.

the southerly direction to facilitate surface runoff. The runoff, both rainfall

and suspended soil, was collected in a clean 1-gal amber glass bottle

this side. The soil in the side where the runoff was collected was left

and filter were sent to the laboratory for analysis.

undisturbed for the duration of the study. Soil box runoff samples were

collected after each rain event that had sufficient intensity and volume to

produce surficial runoff. These samples were filtered, and both the filtrate

The inside of each section was lined with aluminum sheeting and filled with

Each sampler was set up in a north-south orientation and inclined slightly in

secured to one of the sampler legs. Four times during the study, surficial soil

samples were taken from one side of the sampler and analyzed for the same

suite of pesticides as in the rain. No runoff samples were ever collected from

acetate. All the rinses were collected in the 1-gal amber glass solvent bottle

were placed on cleaned, 1-gal amber glass solvent bottles, and the

27-cm diameter stainless steel buckets.

that the funnel rested on and drained in to.

Four agricultural sites were located at the four compass points

2002–2004 Sampling (Wet and Dry Deposition)

Objectives (2002–2004)

To provide a better determination of the contribution of atmospheric deposition, both wet (precipitation) and dry (gaseous and particle), of airborne organophosphorus insecticides and other pesticides to the overall pesticide loading to the San Joaquin River (SJR) area.

In 2002, the sampling sites were changed and distributed over a larger study area. The two sampling sites with autosamplers (sites 8 and 9) were retained. Teflon-lined funnels were located at two sites on the west side of the SJR in predominantly mixed agricultural areas—row crops and orchards (sites 10 and 11); at one site in a rural residential area (site 12), and another at a small rural airport (site 13). Dry as well as wet deposition were collected using the same sampler.

Soil boxes were added to two sites to compare the following: the pesticide concentrations in rainfall with that of runoff from soil; the concentrations in runoff with those on the surface soil mobilized by the rainfall runoff (suspended sediment); and the concentrations on dry deposition collected on the soil (a more natural collection surface) with those of the funnels.

EXPLANATION

McHenry storm drain watershed

Atmospheric deposition

January 2001, Precipitation

▲ Storm drain

Citrus and subtropical

Confined feeding operation

Grain and hay

Mixed agriculture

1. Modesto Irrigation District lateral #4 (373750121092601

2. Turlock Irrigation District lateral #3 (373228120551201)

5. Cadoni Rd. lift station at Modesto (373725120543701

6. Bowen and Aloha St. at Modesto (374028120594301)

3. Tully Rd. near Modesto (374351121004701)

7. McHenry storm drain at Bodem St.

(373847120590801. Runoff)

2001–2004, Wet/Dry Autosampler

(373834121000601)

(373841120504801)

2002-2004, Wet/Dry Sampler

Analytical Methods

Funnel collector at site 11

Soil box collecting runoff

4. WWTP rooftop at Modesto (373637121004601)

8. Modesto Irrigation District rooftop at Modesto

9. Modesto Irrigation District gage at Albers Rd.

10. Westley rain gage at pump building near lateral 6 North

11. Newman rain gage at wasteway levee near Draper Rd

12. Turlock rain gage near Idaho Rd. (372713120534901)

13. Turlock Airport rain gage (372857120414001)

The method used for rain and surface-water samples

pesticide degradates isolated onto a 0.5-g C-18 solid phase

extraction (SPE) cartridge, then eluted with 2 mL of ethyl

operated in the selected ion monitoring (SIM) mode as

described in Sandstrom and others (2001). The analyses

included selected analytes described in Zaugg and others

Dry or bulk deposition samples were shake-extracted with

(1) 30% ethyl acetate (EtOAc) in hexane in a separatory

funnel or (2) dichloromethane (DCM) in the sample bottle(

(DryDisk) membrane. All extracts were dried using Na₂SO₂

and concentrated by Kuderna-Danish (K-D) distillation and

followed by DCM isolation by pouring through a Teflon

nitrogen gas evaporation to 0.5–1.0 mL. Extracts were

introduced to either (a) stacked 0.5-g C-18 silica over 1-

0.5-g graphitized carbon SPE column eluted with 13 mL

and solvent exchange to toluene. Three perdeuterated

PAH internal injection standards were added during N₂

Florisil SPE columns eluted with 6 mL ethyl acetate or (b) a

50% DCM/EtOAc. Extracts were concentrated by micro-K-D

evaporation to 0.5 mL final volume. Extracts were analyzed

by GC/EIMS-SIM for 64 pesticides and degradates using

Suspended sediment samples were extracted using three

10-minute static cycles with 25% acetone/DCM at 100°C

under pressurized conditions. Extracts were subsequently

prepared and analyzed similarly to the dry deposition

samples with graphitized carbon SPE cleanup.

conditions given in Sandstrom and others (2001).

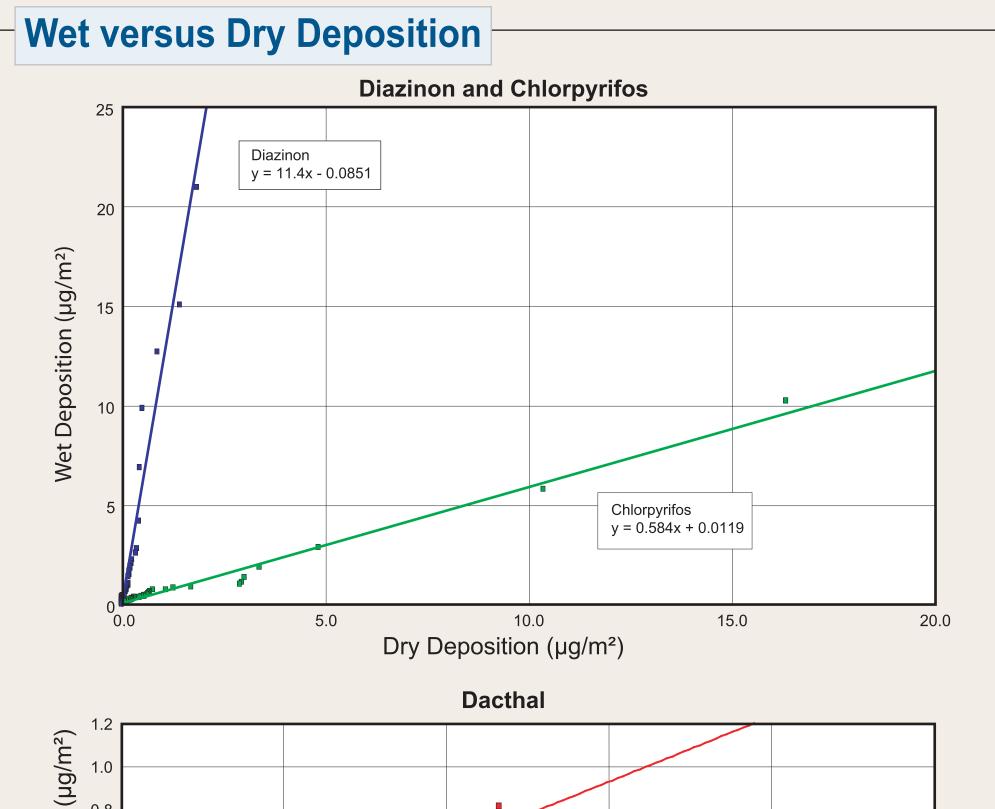
determined a subset of 41 parent pesticides and 23

acetate. The samples were analyzed by GC/EIMS

Dry Deposition and Soil Box

Detection Frequency in Rainfall





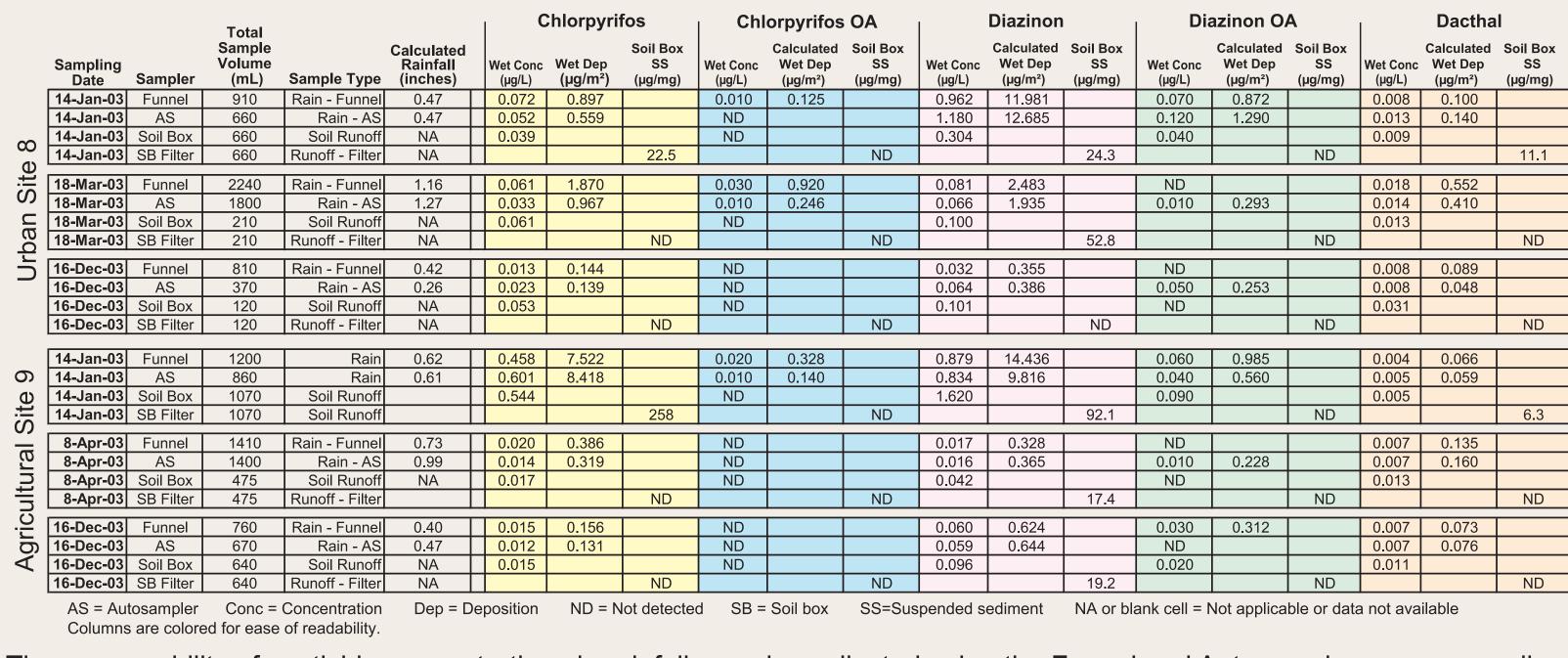
Graphs show the relative importance of wet versus dry deposition during the study period. For those compounds with low Henry's law (H) values, such as diazinon, rainfall was a more significant source of depositional loading to the ground than dry deposition. For those compounds with high Henry's law values, such as chlorpyrifos, dry deposition is more important. Dacthal has a Henry's law value between diazinon and chlorpyrifos, and both wet and dry deposition are nearly equivalent.

Dry Deposition (µg/m²)

		_	1		
Chlorpyrifos	3.34	0.00307	1.1	3.78	
Diazinon	8.0	0.197	0.04	2.76	
Dacthal	14.5	0.0015	0.219	3.75	
Values at 25°C.					
ubcooled liquid phase vapor pressure; S_L , water solubility; K_{OC} , soil absorbtion coefficient; H , Henry's law value)					

P_L (mPa) S_L (mol/m³) H (Pa m³/mol) log K_{oc}

Wet Deposition versus Runoff



The comparability of pesticide concentrations in rainfall samples collected using the Funnel and Autosampler were generally good, although the total volume of rainfall collected by each sampler was often different. The same pesticides detected in rainfall usually were detected in the soil-runoff water, with a few exceptions. The pesticide concentrations in the soil box runoff water were generally similar to those in the rainfall. Very few pesticides were detected on the soil box suspended sediments.

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Summary: 2002–2004 Sampling

- Throughout this 2.5-year study, a wide variety of pesticides were detected in both wet and dry atmospheric deposition. The suite of pesticides detected in rainfall was similar to that in the 2001 study.
- The significance of wet deposition versus dry deposition appears to be closely related to the Henry's law value of each compound, although the mass deposited by dry deposition takes place over a much longer time frame than by wet deposition.
- The soil box results showed that many of the pesticides present in the dissolved phase runoff also were detected in the rainfall and at similar concentrations.
- In the soil box runoff, very few pesticides were detected on the suspended sediments.
- Pesticides in atmospheric deposition can usually be correlated to the proximity of the sampler to application areas as well as to the timing and amount of pesticide used, but not always.

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